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Reactive routes to flame retard some chain-growth polymers: synthetic strategies and characterization techniques

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Polymers are increasingly being used in domestic, commercial and public environments as components of fabrics, surface coatings and moulded articles. Most of these polymeric components are synthetic, are based on hydrocarbon intermediates, and are highly flammable, thus resulting in unwanted fires. Fire fatalities are essentially due to the evolved smoke and toxic gases, exacerbated in some cases by poisonous fumes emitted from synthetic organic polymers. In addition, many of the thermoplastic materials tend to melt and flow under heat/fire, and this can constitute a very serious secondary hazard in fire scenarios involving them. Combustion of polymeric materials is a complex phenomenon that involves the solid phase, gaseous phase and the interphase.

Successful strategies to reduce the flammability of a polymeric material involve breaking into the complex stages of the combustion cycle at one or more stages to reduce the rate and/or change in the mechanism of combustion at that point. From a practical point of view, this is achieved either by the mechanical blending of a suitable flame retardant compound with the polymeric substrate (i.e. as an *additive*) or by the chemical incorporation of the flame retardant into the polymeric molecule by a simple copolymerization or by chemical modification of the preformed polymer (i.e. as a *reactive*)¹.

For the past several years we have been involved in the flame retardation of some commercially important chain-growth polymers, such as polystyrene, polymethyl methacrylate, polyacrylonitrile, etc., through a reactive strategy, owing to some obvious advantages²⁻⁴. These include: low levels of modification are sufficient; the modifying groups are chemically attached and therefore less likely to be lost during subsequent service; the modifying groups can be more readily molecularly dispersed through the polymer; etc. In the present paper, we present some synthetic strategies that we have found successful in chemically modifying, primarily, some styrenic and acrylic polymers with phosphorus-containing moieties.

The characterization techniques that we have employed included: spectroscopic, chromatographic, thermal/thermo-oxidative, calorimetric, and some hyphenated techniques. The wealth of information gathered through the above analytical methods was then used to formulate mechanistic aspects of flame retardation in the modified systems, and to explain the *structure-property* relationships in these materials, at a molecular level. Generally, it was found that P-containing groups were found to be exerting components of mechanisms in both phases, i.e. in the condensed phase and in the vapour-phase, in various degrees. Furthermore, phosphorus-containing acidic species, obtained through an early cracking of pendent phosphonate groups were found to be predominantly responsible for enhanced char production, especially, in the case of typically char-forming polymers, such as, polyacrylonitrile.

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